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Application of the unitary group approach to evaluate spin density for configuration interaction calculations in a basis of S^2 eigenfunctions

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Abstract

We present an implementation of the spin-dependent unitary group approach to calculate spin densities for configuration interaction calculations in a basis of spin symmetry-adapted functions. Using S^2 eigenfunctions helps to reduce the size of configuration space and is beneficial in studies of the systems where selection of states of specific spin symmetry is crucial. To achieve this, we combine the method to calculate $U(n)$ generator matrix elements developed by Downward and Robb (*Theor. Chim. Acta* 1977, 46, 129) with the approach of Battle and Gould to calculate $U(2n)$ generator matrix elements (*Chem. Phys. Lett*. 1993, 201, 284). We also compare and contrast the spin density formulated in terms of the spin-independent unitary generators arising from the group theory formalism and equivalent formulation of the spin density representation in terms of the one- and two-electron charge densities.

KEYWORDS
configuration interaction, configuration state function, quantum chemistry, spin density, unitary group approach

1 | INTRODUCTION

The unitary group approach (UGA) in quantum chemistry was pioneered by Paldus in 1974,[1] with practical algorithms including the most famous graphical approach by Shavitt,[2,3] having been developed in the following years. It offered a simple and straightforward way of evaluating the spin-less generator matrix elements (ME) using implicit Gelfand–Tsetlin basis[4,5] and was suitable for calculating many-electron wavefunction expectation values for spin-independent Hamiltonians.[6] The growing demand for relativisitc corrections and other spin dependent properties in wavefunction methods inspired the subsequent development of spin-dependent generator ME in 80–90s by the several groups of authors[7–23] and the latest work in this field is actually quite recent.[24] In particular, a theory for spin dependent operators formulated entirely within the unitary group formalism has been developed by Gould, Chandler, Paldus, and Battle.[7–15] As we shall discuss, the final formulae are easy to implement and are based on spin-independent $U(n)$ and well-known $U(2)$ generator ME in terms of the Gelfand–Tsetlin implicit basis. As a special, zero-order case, this theory provides a rather simple way for calculating spin density.[13,15,25]

An obvious approach to spin density calculation with configuration interaction (CI) wavefunction would be to use the precomputed spin-dependent generator ME. The general single-particle reduced density operator (in a 2×2 matrix form) is given by[13]:

$$\hat{\rho}(r,r')_{\mu\nu} = \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')E_{jv,i\mu}, \tag{1}$$

and the electron spin density operator is defined by:

$$\hat{\rho}^S(r,r') = \frac{1}{2}\left(\hat{\rho}(r,r')_{1/2,1/2} - \hat{\rho}(r,r')_{-1/2,-1/2}\right). \tag{2}$$

The spin density can be most easily obtained using Slater determinants (SD) where the ME are a simple sum of spin components. However, the use of S^2 eigenfunctions to give configuration state functions (CSF) is essential in studies of transition metals and other compounds for which states with high spin quantum number play an important role. They allow for selective calculation of electronic states with the given spin symmetry as well as reducing the configuration space. Generator ME are, however, more difficult to formulate in this case. In this article, we use the UGA-based algorithm as described by Robb, Downward, and Hegarty,[26,27] and extend it to the spin-dependent case using the approach of Gould et al.,[7] to compute spin densities using Equation 2 in a basis of S^2 eigenfunctions.

In their recent paper on the formulation of spin densities for the spin-adapted open-shell coupled-cluster method, Datta and Gauss suggested that formulae by Gould et al.[7] were rather too complicated and indeed no implementation has been reported so far.[28] (However, note that Battle has published an implementation of the Gould formalism in his PhD thesis.[29]) Instead, Datta and Gauss used a compact formulation for spin density from the paper by Luzanov,[30] given in terms of one- and two-particle charge density matrices R_{ij} and $R_{ij,kl}$ (the same formula has been later used by Shiozaki and Yanai in Ref. [31]). For an N-electron state with spin S and $M=+S$ one has

$$Q_{ij} = \frac{1}{S+1}\left(\left(2-\frac{N}{2}\right)R_{ij} - 2\sum_{k=1}^{n} R_{ki,jk}\right). \tag{3}$$

This expression is reformulated in the same paper in terms of the $U(n)$ spin-independent generator ME as

$$Q_{ij} = \frac{1}{S+1}\left(\left(2+n-\frac{N}{2}\right)\langle\Psi|E_{ij}|\Psi\rangle - \sum_k \langle\Psi|E_{ik}E_{kj}|\Psi\rangle\right). \tag{4}$$

Here, Q_{ij} is a spin density matrix element, related to Equation 2 by the following definition of spin density arising from a given molecular wavefunction Ψ:

$$\begin{aligned}\rho^S(r) &= \langle\Psi|\hat{\rho}^S(r,r)|\Psi\rangle = \frac{M}{2S}\sum_{i,j=1}^{n}\phi_i^*(r)\phi_j(r)Q_{ij} \\ &= \frac{1}{2}\sum_{i,j=1}^{n}\phi_i^*(r)\phi_j(r)\langle\Psi|E_{j1/2,i1/2} - E_{j-1/2,i-1/2}|\Psi\rangle.\end{aligned} \tag{5}$$

Such an expression for a one-electron property may at first seem rather strange since the difference of the one-particle spin-dependent generators is defined via a contraction over the two-body spin-independent generators. We shall show that the Luzanov formula (Equation 4) in fact corresponds to an intermediate result obtained by Gould et al. Indeed, Gould obtains the same result which he then simplifies by applying group theory (i.e., spin coupling) techniques thereby lifting the necessity to perform explicit contraction over the two-particle generator ME. It is, however, significant that Luzanov et al. obtained Equations 3 and 4 in framework of a fundamentally different formalism from the UGA approach by Gould et al.[32] Our main objective is to discuss our implementation of the formulae for spin-dependent generators within the Robb, Downward, and Hegarty formulation.[26,27] However, as a secondary objective of this article, we shall give a unified overview of Gould's spin-dependent UGA formalism and compare it with the reduced density matrix formalism by Luzanov et al.

This article is structured as follows. In theory section we give an overview of the spin-dependent UGA formalism of Gould et al. and reduced density formalism of Luzanov et al., emphasizing the resulting relation of the one-electron spin density to the one- and two-electron charge density. In implementation and test case section we describe the algorithm to calculate the spin-dependent generator ME implemented within the Robb, Downward and Hegarty formulation.[26,27] A model calculation of CASSCF spin density for a metal-containing complex is given as a demonstration. Finally, in discussion and conclusion section we provide a brief discussion of the implemented algorithm and the two formalisms described in theory section.

2 | THEORY

2.1 | Spin dependent UGA

Initially applied in the context of nuclear physics by Moshinsky,[33] the unitary group representation theory has been used as a formalism in electronic structure CI calculations since the seminal work of Paldus in 1974.[1] He exploited the fact that spin-independent electronic Hamiltonian can be expressed as

$$H = \sum_{i,j}\langle i\,|\,z\,|\,j\rangle E_{ij} + \frac{1}{2}\sum_{i,j,k,l}\langle ij\,|\,v\,|\,kl\rangle\left(E_{ik}E_{jl} - \delta_{jk}E_{il}\right), \tag{6}$$

in terms of the spin-independent generator operators E_{ij}, given as the sum of products of annihilation and creation operators:

$$E_{ij}=\sum_{\mu} X^{\dagger}_{i\mu}X_{j\mu}, \tag{7}$$

where i and j denote orbitals $(i,j=1,\ldots,n)$ and μ denotes the spin of electron $(\mu=\alpha,\beta)$. Paldus further noticed that those generator operators possess all the properties of the unitary $U(n)$ group generators. Hence, the existing unitary group algebra was adopted for evaluating the Hamiltonian ME. The basis set for the finite dimensional irreducible representations of the unitary groups as originally discovered by Gelfand–Tsetlin[4,5] and later developed by Baird and Biedenharn[34] was used as the N-electron CI basis set. The relevant formulae for the $U(n)$ (spin-free) E_{ii} and $E_{i,i+1}$ generator ME were provided, with the remaining off-diagonal E_{ij} ME to be evaluated using the simple commutation relations.[1] For the formulae and the details one should refer to the 1974 Paldus original paper as well as to the several excellent pedagogical reviews indicating historical development of the subject.[35–38]

To keep our presentation as self-contained as possible, we review the main ideas. First, one needs the various graphical tableaus used to define the Gelfand–Tsetlin (GT) basis set. We will describe the original Gelfand tableau, and the easier-to-handle Paldus tableau. Each finite-dimensional irreducible representation of $U(n)$ is uniquely specified by the n integers m_{in}: $(m_{1n},m_{2n},\ldots,m_{nn})$, ordered such that $m_{1n}\geq m_{2n}\geq\ldots\geq m_{nn}$. An individual basis vector of this irreducible representation carrier space is given by a triangular pattern, named Gelfand taleau:

$$\begin{bmatrix} m_{1n} & m_{2n} & m_{3n} & \cdots\cdots\cdots & m_{nn} \\ & m_{1,n-1} & m_{2,n-1} & \cdots\cdots\cdots & m_{n-1,n-1} \\ & & m_{1,n-2} & \cdots\cdots & m_{n-2,n-2} \\ & & & \cdots\cdots\cdots\cdots & \\ & & & m_{12} & m_{22} \\ & & & & m_{11} \end{bmatrix}, \tag{8}$$

where the first row labels the given irreducible representation and the remaining rows contain integers that satisfy the "betweenness" conditions:

$$\begin{cases} m_{i,j+1}\geq m_{i,j}\geq m_{i+1,j+1} \\ i\leq j=1,\ldots,(n-1) \end{cases}, \tag{9}$$

and label the irreducible representations of the $U(n-1),U(n-2),\ldots,U(1)$ sub-groups. Due to the ordering, the first row (and, therefore, the corresponding irreducible representation) can be labeled by the sum of its elements, also known as the *highest weight*: $\lambda_n=\sum_i m_{in}$. Gelfand tableaus uniquely specify basis vectors and give an opportunity for their straightforward construction in "lexical" order.

In CI calculations one has a single particle basis set of $(2n)$ spinorbitals $|i\rangle|\mu\rangle$, $\left(i=1,\ldots,n;\mu=\pm\frac{1}{2}\right)$. Then, one has the associated $(2n)^2$ operators $X^{\dagger}_{i\mu}X_{jv}$ corresponding to the $U(2n)$ group. Due to the spin-independent nature of the Hamiltonian (Equation 6), instead of the $U(2n)$ group, its subgroup $U(n)\times U(2)$ can be used. Further, if the direct product representation of $U(n)\times U(2)$ is to be totally antisymmetric (which is the case of the N-electron problem), then the irreducible representations of $U(n)$ and $U(2)$ must be mutually conjugate. Thus, one needs only the irreducible representation of the orbital $U(n)$ subgroup with the generators given by Equation 7 and one can restrict consideration to those irreducible representations for which the conditions $0\leq m_{in}\leq 2$, $(i=1,\ldots,n)$ and $\sum_{i=1}^{n} m_{in}=N$ (total number of electrons) hold.

In view of this simplification, the somewhat complicated original general formulae for the generator operator ME in terms of Gelfand–Tsetlin basis set were reformulated by Paldus using the simplified $n\times 3$ rectangular tableau:

$$\begin{bmatrix} a_n & b_n & c_n \\ a_{n-1} & b_{n-1} & c_{n-1} \\ & \vdots & \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \end{bmatrix}. \tag{10}$$

The integers a_i, b_i, and c_i specify the number of m_{ji} entries in the ith row having the values 2, 1, and 0, respectively. For example, the first (highest weight) basis vector for a system of three electrons in four orbitals in the two notations will read:

$$\begin{bmatrix} 2 & 1 & 0 & 0 \\ & 2 & 1 & 0 \\ & & 2 & 1 \\ & & & 2 \end{bmatrix} \equiv \begin{bmatrix} 1 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}. \tag{11}$$

Paldus has presented the formulae for the E_{ii} and $E_{i,i+1}$ ME in his original paper in terms of this type of tableau.[1] Specific to the irreps used in electronic structure calculations, described by the Paldus simplified tableau, are also the two subsequent UGA formalisms involving tensor operator

techniques such as the one used by Gould et al. (based on works by Green and Bracken)[39,40] as well as the more recent formalism based on spin-adapted analogues of creation and annihilation operators, developed by Li and Paldus.[24] In addition to Gelfand and Paldus tableaus, another useful pattern called Weyl tableau being the special form of Young tableau has been used by Downward and Robb for an automated computation of the generator ME in terms of GT basis vectors.[26]

As described above, Paldus has derived simple formulae for the $U(n)$ (spin-free) group generator operators ME, providing a simple tool for the CI energy calculations. However, if one wishes to calculate spin-dependent properties such as spin density within the UGA, one must be able to evaluate either the $U(2n)$ group generator operators ME per se (see Equations 1 and 2) or the $U(n)$ adjoint tensor operator Δ ME (a polynomial of degree two in the $U(n)$ generators, see below).

A method to calculate either the $U(2n)$ $E_{j\mu,i\mu}$ ME or the spin densities directly in terms of ME of Δ_{ij}, was developed by Gould et al. in a series of papers.[8–15] The final version of the formulae was given in Ref. [7]. We note that Ref. [12] is in fact an erratum for Refs. [8–10]. Further, importantly, the zero-shift components of $U(2n)$ generators are in error in Ref. [9] so we describe below an alternative approach given in Ref. [14]. This approach, however, still makes use of the vector operator and adjoint tensor operator formalism, given by Gould and Chandler in Refs. [8,9].

In the first paper, the formulae for the $U(n)$ generator ME were rederived using the properties of a *vector operator* of $U(m)$, defined as a collection of operators $\Psi_i (i=1,\ldots,m)$ that satisfy the commutation relation[8]:

$$[E_{ij},\Psi_k]=\delta_{kj}\Psi_i. \tag{12}$$

The $U(m+1)$ generators $E_{i,m+1} (i=1,\ldots,m)$ then constitute a vector operator of $U(m)$ with the components $\Psi(m)_i=E_{i,m+1}$. With V being the (fundamental) finite dimensional vector representation of $U(m)$, Ψ_i transforms like its basis vectors e_i:

$$E_{ij}e_k=\delta_{kj}e_i. \tag{13}$$

If we then denote an arbitrary finite dimensional irreducible representation as $V(\boldsymbol{\lambda})$ and v is a $U(m)$ diagonal generators ($E_{ii} (i=1,\ldots,m)$) eigenvector, $v \in V(\boldsymbol{\lambda})$, it becomes evident that $\Psi_k v$ transforms like the vector $e_k \otimes v$ in the tensor product representation $V \otimes V(\boldsymbol{\lambda})$. This representation decomposes into a direct sum of three irreducible representations:

$$V \otimes V(\boldsymbol{\lambda})=\oplus_{r=1}^{3} V(\boldsymbol{\lambda}+\boldsymbol{\Delta}_r), \tag{14}$$

due to restrictions imposed by the form of the highest weight $\boldsymbol{\lambda}$ allowed for the N-electronic problem.[8] It follows that Ψ_i acting on $V(\boldsymbol{\lambda})$ may be resolved into a sum of three shift components, out of which only two actually survive according to Gelfand tableau lexicality rules:

$$\Psi(m)_i=\sum_{r=1}^{2}\Psi\begin{pmatrix} r \\ m \end{pmatrix}_i, \tag{15}$$

which, in terms of Paldus tableau, shift the Paldus labels of the group $U(m)$ according to

$$\Psi\begin{pmatrix} r \\ m \end{pmatrix} : [a_m,b_m,c_m] \rightarrow [a_m,b_m,c_m]+\delta_r, \qquad r=1,2, \tag{16}$$

where δ_r dentotes the allowed shifts:

$$\delta_1=[0,1,-1], \qquad \delta_2=[1,-1,0]. \tag{17}$$

Similarly, one can resolve the $U(m)$ *contragredient vector operator* $\Psi^{\dagger}(m)_i=E_{m+1,i}$ with shift components, altering Paldus labels of the group $U(m)$ according to

$$\Psi^{\dagger}\begin{pmatrix} r \\ m \end{pmatrix} : [a_m,b_m,c_m] \rightarrow [a_m,b_m,c_m]-\delta_r, \qquad r=1,2. \tag{18}$$

Importantly, each shift component $\Psi\begin{pmatrix} r \\ m \end{pmatrix}_{i\leq m-1}$ is also a component of a vector operator with respect to $U(m-1)$ and can be further decomposed into $U(m-1)$ shift components:

$$\Psi\begin{pmatrix} r \\ m \end{pmatrix}_i=\sum_{k=1}^{2}\Psi\begin{pmatrix} r & k \\ m & m-1 \end{pmatrix}_i, \tag{19}$$

and so forth up to the $U(i)$ shift components. Thus, an operator of the form $E_{m,m+p} (m<m+p \leq n)$ may be decomposed into a multiple sum of shift components that simultaneously alter the Paldus labels of the subgroups $U(m+p-1), U(m+p-2),\ldots,U(m)$ and leaving labels of the subgroups $U(n),\ldots,U(m+p),U(m-1),\ldots,U(1)$ untouched:

$$E_{m,m+p}=\sum_{i_m=1}^{2}\sum_{i_{m+1}=1}^{2}\cdots\sum_{i_{m+p-1}=1}^{2}\Psi\begin{pmatrix} i_{m+p-1} & \cdots & i_{m+1} & i_m \\ m+p-1 & \cdots & m+1 & m \end{pmatrix}_m. \tag{20}$$

Gould and Chandler use these properties of the vector and contragredient vector operators and derive explicit formulae for both elementary and nonelementary generator operators in terms of their product $\Phi(m)=\Psi^{\dagger}(m)\Psi(m)$, which possesses an important property of being decomposable into a product of its segments:

$$\Phi\begin{pmatrix} i_{m+p-1} & \cdots & i_m \\ m+p-1 & \cdots & m \end{pmatrix}=\Phi\begin{pmatrix} i_{m+p-1} & \cdots & i_r \\ m+p-1 & \cdots & r \end{pmatrix}\Phi\begin{pmatrix} i_{r-1} & \cdots & i_m \\ r-1 & \cdots & m \end{pmatrix}\xi^{(r)}_{i_r,i_{r-1}}, \tag{21}$$

where $\xi^{(r)}_{i_r,i_{r-1}}$ is a coefficient that is equal to one in the case when $i_r=i_{r-1}$ and has a simple formula in terms of Paldus labels in the other cases.[8] This gives rise to the relatively easy-to-evaluate segment formulae for the general E_{ij} ME.

In their following paper, Gould and Chandler introduced the formalism of *adjoint tensor operators* of $U(n)$ (with the formal theory given in Ref. [41]) that transform like the basis vectors of the n^2-dimensional adjoint representation of $U(n)$.[9] Those basis vectors are in fact elementary matrices $e_{ij},(i,j=1,\ldots,n)$ with one in the (i, j) position and zeros elsewhere. Generators E_{ij} then satisfy:

$$[E_{ij}e_{kl}]=\delta_{kj}e_{il}-\delta_{il}e_{kj}, \tag{22}$$

and an adjoint tensor operator X transforms according to:

$$[E_{ij}X_{kl}]=\delta_{kj}X_{il}-\delta_{il}X_{kj}. \tag{23}$$

The authors further notice that the $U(2n)$ generators transform as the representation $[Adj]\otimes[Adj]$ under commutation with its subgroup $U(n)\times U(2)$. Since $U(2n)$ generators $E_{i\mu,j\nu}$ satisfy

$$[E_{i\mu,j\nu},E_{k\rho,l\tau}]=\delta_{kj}\delta_{\rho\nu}E_{i\mu,l\tau}-\delta_{il}\delta_{\mu\tau}E_{k\rho,j\nu}, \tag{24}$$

and generators of the $U(n)\times U(2)$ subgroup commute, one obtains

$$\left[\sum_{\mu=1}^{2}E_{i\mu,j\mu},E_{k\mu,l\nu}\right]=\delta_{kj}E_{i\mu,l\nu}-\delta_{il}E_{k\mu,j\nu}, \tag{25}$$

$$\left[\sum_{i=1}^{n}E_{i\mu,i\nu},E_{i\rho,j\tau}\right]=\delta_{\rho\nu}E_{i\mu,j\tau}-\delta_{\mu\tau}E_{i\rho,j\nu}. \tag{26}$$

They note further that the adjoint representation of $U(m)$ is equivalent to the representation $V\otimes V^{*}$, where V^{*} is the contragredient vector representation of $U(m)$. With $\{e_i\}_{i=1}^{n}$ and $\{\bar{e}_i\}_{i=1}^{n}$ being the corresponding basis sets, the vectors $e_i\otimes\bar{e}_j$ constitute basis for the adjoint representation, which implies that one may construct a $U(m)$ adjoint tensor operator X_{ij} by coupling the $U(m)$ vector and contragredient vector operators:

$$X_{ij}=\Psi_i\Psi_j^{\dagger}. \tag{27}$$

It was shown above that vector operators can be decomposed into a sum of shift components when acting on an irreducible representation $V(\boldsymbol{\lambda})$. Therefore, the adjoint tensor operator may as well be decomposed into a sum of shift components

$$X_{ij}=\sum_{r}\Psi\begin{pmatrix} r \\ m \end{pmatrix}_i\Psi^{\dagger}\begin{pmatrix} r \\ m \end{pmatrix}_j+\sum_{r\neq l}\Psi\begin{pmatrix} r \\ m \end{pmatrix}_i\Psi^{\dagger}\begin{pmatrix} l \\ m \end{pmatrix}_j, \tag{28}$$

with this equation in a more general and compact notation taking the following form:

$$X_{ij}=X[0]_{ij}+\sum_{r\neq l}X[r,l]_{ij}. \tag{29}$$

For the $U(2n)$ group we have then

$$E_{i\mu,j\nu}=E(0)_{i\mu,j\nu}+E(-)_{i\mu,j\nu}+E(+)_{i\mu,j\nu}, \tag{30}$$

where only the zero-shift component $E(0)_{i\mu,j\nu}$ plays a role for the spin-independent systems and will, therefore, solely be considered in the following.

In the later paper, the zero-shift component was determined by Gould and Paldus as a simple polynomial in the $U(n)$ and $U(2)$ generators.[14] Previously, Gould and Chandler have shown that on an irrep of $U(n)$ with Paldus labels $[a,b,c]$, the $U(n)$ matrix $E=[E_{ij}]_{1\leq i,j\leq n}$ satisfies only the third-order polynomial identity (follows from Equation 14)[8]:

$$E(E-\epsilon_1)(E-\epsilon_2)=0, \tag{31}$$

where $\epsilon_1=1+c$ and $\epsilon_2=n+2-a$. According to the general theory of $U(n)$ adjoint tensor operators,[41] there exist in general at most n independent $U(n)$ zero-shift adjoint tensors, $(E^m)_{ij}$, with $m=0,1,\ldots,n-1$, where polynomials in the $U(n)$ E-matrix are defined recursively according to:

$$(E^{m+1})_{ij}=\sum_k E_{ik}(E^m)_{kj}, \qquad (E^0)_{ij}=\delta_{ij}. \tag{32}$$

As noted above, for the many-electron problem, one has to deal with only three independent zero-shift $U(n)$ adjoint tensor operators: δ_{ij}, E_{ij}, and $(E^2)_{ij}$. For $U(2)$, one can have at most two independent zero-shft adjoint tensor operators: $\delta_{\mu\nu}$ and $E_{\mu\nu}$ and, therefore, taking into account the properties of the $U(2n)$ adjoint tensor operators one can write $E(0)_{i\mu,j\nu}$ as[14]:

$$E(0)_{i\mu,j\nu}=(E^2)_{ij}(\alpha_1 E+\beta_1 I)_{\mu\nu}+E_{ij}(\alpha_2 E+\beta_2 I)_{\mu\nu}+\delta_{ij}(\alpha E+\beta I)_{\mu\nu}, \tag{33}$$

where I denotes a 2×2 identity matrix, and the coefficients α_i,β_i,α, and β are the $U(n)\times U(2)$-invariant operators, depending solely on the $U(n)$ Paldus $[a,b,c]$ labels. Gould and Paldus have then shown in an elegant derivation that Equation 33 reduces to[14]:

$$E(0)_{i\mu,j\nu}=\frac{1}{2}E_{ij}\delta_{\mu\nu}-\begin{cases}0, & S=0\\ \dfrac{\Delta_{ij}\tilde{E}_{\mu\nu}}{2S(S+1)}, & S\neq 0\end{cases}, \tag{34}$$

where S is the system spin, $\tilde{E}_{\mu\nu}$ denote the $SU(2)$ generators:

$$\tilde{E}_{\mu\nu}=E_{\mu\nu}-\frac{N}{2}\delta_{\mu\nu}, \tag{35}$$

with the $E_{\mu\nu}$ ME previously known,[9,34] and Δ is the polynomial of degree two in the $U(n)$ matrix E, also an adjoint tensor operator, with its ME given by:

$$\Delta_{ij}=(E^2)_{ij}+\left(\frac{N}{2}-n-2\right)E_{ij}, \tag{36}$$

with $(E^2)_{ij}=\sum_k E_{ik}E_{kj}$ according to Equation 32, N being the number of electrons in the system and n the number of orbitals in the CI space. To be self-consistent, we provide the formula for the $E_{\mu\mu}$ ME (as we are only interested in $E(0)_{i\mu,j\mu}$ ME to be able to calculate the spin densities). The eigenvalue equations for the diagonal $U(2)$ generators read:

$$E_{11}\left|\begin{matrix}\lambda_1 & \lambda_2\\ & m\end{matrix}\right\rangle=m\left|\begin{matrix}\lambda_1 & \lambda_2\\ & m\end{matrix}\right\rangle, \tag{37}$$

$$E_{22}\left|\begin{matrix}\lambda_1 & \lambda_2\\ & m\end{matrix}\right\rangle=\lambda_1+\lambda_2-m\left|\begin{matrix}\lambda_1 & \lambda_2\\ & m\end{matrix}\right\rangle, \tag{38}$$

where $\lambda_1=m=a+b$ and $\lambda_2=a$, with a and b being the $U(n)$ irrep Paldus labels.

One can stop here and implement Equations 34–38 directly. Moreover, if to substitute Equation 34 into Equations 1 and 2 and apply the formula $S_z=\frac{1}{2}(E_{1/2,1/2}-E_{-1/2,-1/2})$, it turns out that spin density can be directly calculated from the Δ adjoint tensor operator[13]:

$$\hat{\rho}^S(r,r')=\frac{-S_z}{2S(S+1)}\sum_{i,j=1}^{n}\phi_i^*(r)\phi_j(r')\Delta_{ij}. \tag{39}$$

(In reduced density matrix formalism section we will discuss that this directly corresponds to the formula given by Luzanov.[30]) However, based on the adjoint tensor operator formalism briefly described above, Gould and Battle developed simple segment formulae for evaluating Δ_{ij} ME that do not require performing multiple summations over the bilinear terms in Equation 36,[15] which we concisely cover below.

The derivation of the general Δ_{ij} ME is again based on its property as a $U(n)$ adjoint tensor operator to be decomposable into the well-defined shift components[15]:

$$\Delta(n+1)_{ij}=\sum_{\alpha_n}\Delta\begin{pmatrix}n\\ \alpha_n\end{pmatrix}_{ij}, \tag{40}$$

where the shift components alter Paldus labels according to:

$$\Delta\begin{pmatrix}n\\ \alpha_n\end{pmatrix}_{ij}:[a_n,b_n,c_n]\rightarrow[a_n,b_n,c_n]+\epsilon_{\alpha_n}, \tag{41}$$

with the three possible values of ϵ_{α_n}:

$$\begin{aligned}\epsilon_+ &= \delta_1 - \delta_2 = [-1, 2, -1],\\ \epsilon_- &= \delta_2 - \delta_1 = [1, -2, 1],\\ \epsilon_0 &= [0, 0, 0].\end{aligned} \tag{42}$$

However, since we are only considering the zero-shift $E(0)_{i\mu,jv}$ component, only ϵ_0 leads to the nonzero ME.[14,15] Therefore, Δ_{ij} ME are represented here by a single zero-shift component:

$$\Delta(n+1)_{ij} = \Delta \begin{pmatrix} n \\ 0 \end{pmatrix}. \tag{43}$$

First of all, Gould and Battle considered the diagonal matrix elements Δ_{ii} and derived the following recursive relation in terms of the Paldus labels, based on the general formulae for $U(n)$ E_{ij} generators and Equation 36:

$$\Delta \begin{pmatrix} n \\ 0 \end{pmatrix}_{ii} = \frac{1 + b_{n+1} + \Delta b_{n+1}}{1 + b_{n+1}} \Delta(n)_{ii}, \tag{44}$$

where $\Delta b_m = b_m - b_{m-1}$ (with $\Delta b_1 = b_1$). Here, they used the preliminarily derived formula for the $U(m)$ invariant operator $\Delta(m)_{mm}$:

$$\Delta(m)_{mm} = -\frac{\Delta b_m}{2}(1 + b_m + \Delta b_m). \tag{45}$$

Equations 44 and 45 immediately sugest a recursive (segment) formula for a general $\Delta(n)_{mm}$ ME:

$$\left(\begin{matrix} p_n \\ [P]_{n-1} \end{matrix} \middle| \Delta(n)_{mm} \middle| \begin{matrix} p_n \\ [P]_{n-1} \end{matrix} \right) = \Delta \begin{pmatrix} n-1 & \dots & m \\ 0 & \dots & 0 \end{pmatrix}_{mm} = T_m(0)\, \Delta^* \begin{pmatrix} n-1 & \dots & m+1 \\ 0 & \dots & 0 \end{pmatrix}_{mm} = T_m(0) \prod_{r=m+1}^{n-1} T^{(r)}_{0,0} \quad T^{(n)}(0), \tag{46}$$

with the segments given as:

$$\begin{aligned} T_m(0) &= -\frac{\Delta b_m}{2}(1 + b_m + \Delta b_m),\\ T^{(r)}_{0,0} &= \frac{1 + b_r + \Delta b_r}{1 + b_r},\\ T^{(n)}(0) &= \frac{1 + b_n + \Delta b_n}{1 + b_n}. \end{aligned} \tag{47}$$

In Equation 46, we have introduced a shorthand representation for the GT basis vector, where $p_n = [a_n, b_n, c_n]$ and $[P]_{n-1}$ is an allowed Paldus tableau for the $U(n-1)$ subgroup. It should also be understood above that $T^{(n)} = 1$ if $m = n$ and $\prod_r T^{(r)}_{0,0} = 1$ if $m > n-2$.

Having found the formula for the Δ_{ii} ME, it is straightforward to obtain the off-diagonal ME using the commutation relation that is satisfied since $\Delta(n)_{ij}$ forms a component of a $U(n)$ adjoint tensor operator:

$$\Delta(m)_{m,m+p} = [E_{m,m+p}, \Delta_{m+p,m+p}]. \tag{48}$$

Calculation of $\Delta_{m,m+p}$ with the use of the above expression involves an in principle expensive matrix commutator evaluation, but due to the properties of both operators, at most two intermediate states can occur in the summation.[15] This allowed Gould and Battle to derive an analytical segment formula in terms of Paldus labels, which for the non-zero raising generator ME reads:[7,15]

$$\left(\begin{matrix} p_n \\ \vdots \\ p_{m+p} \\ p_{m+p-1} + \delta_{i_{m+p-1}} \\ \vdots \\ p_m + \delta_{i_m} \\ [P]_{m-1} \end{matrix} \middle| \Delta_{m,m+p} \middle| \begin{matrix} p_n \\ \vdots \\ p_{m+p} \\ p_{m+p-1} \\ \vdots \\ p_m \\ [P]_{m-1} \end{matrix} \right) = V(0, i_{m+p-1})\, \Delta^* \begin{pmatrix} n-1 & \dots & m+p+1 \\ 0 & \dots & 0 \end{pmatrix} N \begin{pmatrix} m+p-1 & \dots & m \\ i_{m+p-1} & \dots & i_m \end{pmatrix}, \tag{49}$$

where $i_k = 1, 2$ (see Equation 17) and the new terms read:

$$V(0, i_{m+p-1}) = \frac{1}{2}(-1)^{i_{m+p-1}}(b_{m+p} + 2\Delta b_{m+p} + 2i_{m+p-1} - 2), \tag{50}$$

and

$$N\begin{pmatrix} m+p-1 & \dots & m \\ i_{m+p-1} & \dots & i_m \end{pmatrix} = \omega\left(\frac{(1+b_m)(b_m+4-2i_m)}{(1+b_{m-1})(1+b_{m+p})}\right)^{\frac{1}{2}} \prod_{r=m+1}^{m+p-1} (1+b_r)^{-|i_r-i_{r-1}|}\left(\frac{b_r+3-i_r}{b_r+2-i_r}\right)^{\frac{\Delta b_r}{2}}, \tag{51}$$

being the usual $U(n)$ raising generator ME,[8] with its phase given as

$$\omega = \prod_{q=m+1}^{m+p-1} S(i_{q-1}-i_q)(-1)^{\sigma_{q-1}^{i_{q-1}}}, \tag{52}$$

with $S(x) = sign$ of x ($S(0)=1$) and

$$\sigma_q^1 = (1+c_q-c_{q+1}), \qquad \sigma_q^2 = (a_{q+1}-a_q). \tag{53}$$

2.2 | Reduced density matrix formalism

One of the central expressions of spin dependent UGA section is Equation 39—it presents the spin density operator as a function of a $U(n)$ adjoint tensor operator Δ, being a second-order polynomial in the $U(n)$ generators (Equation 36). Spin density appears, therefore, to be a function of contracted one- and two-electron spin independent generators with the spin dependence being confined in a simple coefficient in front of the summation:

$$\rho^S(r) = \frac{M}{2S(S+1)} \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r)\left(\left(2+n-\frac{N}{2}\right)\langle\Psi|E_{ij}|\Psi\rangle - \sum_k \langle\Psi|E_{ik}E_{kj}|\Psi\rangle\right). \tag{54}$$

Derivation of this expression as given by Gould et al. bears a purely group theoretical nature.

An identical expression in terms of the one- and two-electron charge densities has been, however, derived by Whyman et al. based on the density matrix formalism.[32] Its derivation was just one of the results in a wider study of separation of the spin variables in the two-particle reduced density matrices and conditions of N-representability. Its importance per se has been later emphasized by Harriman,[42] followed by the same authors generalizing this expression for the arbitrarily high-order reduced density matrices.[43,44] In the expression they obtained the spin density operator was given as:

$$Q = \frac{M}{S(S+1)}\left(\left(2-\frac{N}{2}\right)R_1 - 2Sp_2R'_{12}\right), \tag{55}$$

where R_1 and R_{12} are the one- and two-electron charge density operators respectively, Sp_2 defines reduction with respect to the second electron coordinate and prime denotes transposition in the second pair of spatial coordinates. The matrix element form of Equation 55 is given by Equation 3 for the case where $M=+S$. Luzanov has later reformulated this expression by simply expanding the charge density matrix elements in terms of the unitary group generators,[30] resulting in Equation 4, which, substituted in Equation 5 results in Equation 54.

In this way, derivation of the segment formulae allowing for direct evaluation of the Δ_{ij} ME in terms of the Gelfand–Tsetlin basis done by Gould and Battle (Equations 40–53) can be viewed simply as an extension to the formula obtained by Whyman et al. that avoids explicit contraction over the two-electron generator terms thereby making computation of spin density cheaper. We also acknowledge an elegant derivation of Equation 54 given by Gidofalvi and Shepard in the appendix of Ref. [45] which they then also simplify using the properties of the graphically contracted functions. We however note that the formulation by Whyman et al., while more expensive computationally, is more widely applicable as it only utilizes density matrices and does not need the UGA techniques to be implemented.

3 | IMPLEMENTATION AND TEST CASE

In this section, we describe our implementation of the spin-dependent UGA used to compute $E_{i\mu,j\mu}$ ME in the development version of Gaussian[46] and provide a short test case of spin density evaluation for electronic states of a chromium complex with different multiplicities in a basis of S^2 eigenfunctions. In accordance with the general notation of this article, we will use n to denote the number of orbitals and N-the number of electrons in the active space.

In their original paper, Gould and Battle described a possible implementation of their segment formulae in frames of Shavitt's graphical method,[15] which would involve repeated application of multiple tests to determine the shift type of the final GT state for all the non-vanishing $U(2n)$ generator ME. In our implementation, we followed what seems to us as a simpler strategy.

By applying Robb and Downward approach that makes use of the Weyl tableau formalism,[26] we first calculate the $U(n)$ E_{ii} and $E_{i,i-1}$ (elementary) generator ME. A two-column Weyl tableau is especially suited for an automated computation of the $U(n)$ elementary generators since every basis function can be coded as a short string of N integers, and the only pair of configurations leading to a nonzero $E_{i,i-1}$ ME will be identical except for a single integer in the same position, which will be an i for the "left" and an i – 1 for the "right" configuration. This allows for an intuitive

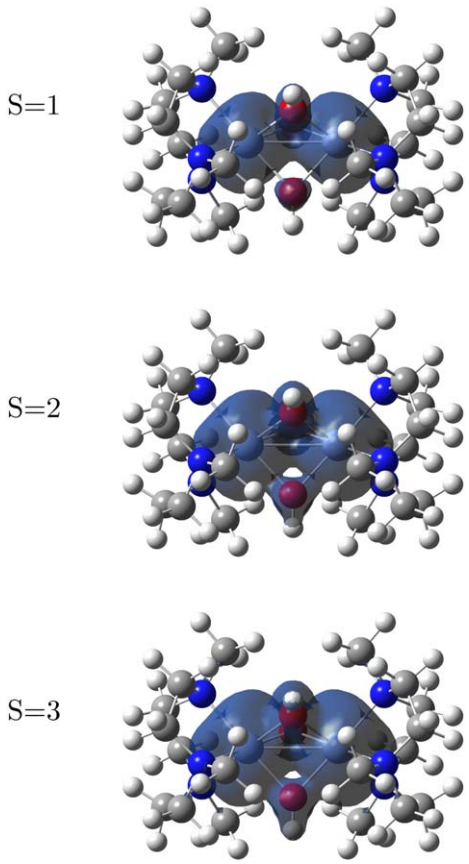

FIGURE 1 Spin density for the three different spin states of the Kremer's chromium dimer complex, labeled by their total spin quantum number, evaluated at the CASSCF theory level using spin-adapted GT configuration state functions. Isovalue of 0.0004 was used for the density surface. Atom coloring notation: chromium-purple; oxygen-red; nitrogen-blue; carbon-gray, hydrogen-white. We note that in figure 1 of Ref. [47] the hydrogen atoms on terminal ligands have been omitted

algorithm that computes generator ME as the basis vectors are being created in successive levels (defined by their total weights) by addition of a unit to all the possible positions of the previous level tableaus that do not violate the shift rules (Equation 17).

For those pairs of the GT basis vectors that give nonzero $U(n)$ elementary generators, we also calculate the Δ_{ii} and $\Delta_{i,i-1}$ ME using Equations 46 and 49, obtaining all the necessary input terms via a subroutine that transforms a given Weyl tableau into a Paldus tableau, and construct the corresponding $U(2n)$ generators using Equation 34 in a straightforward manner. Computation of the lower-diagonal part of the generator matrices is sufficient due to the well-known relation $E_{ij}^{\dagger}=E_{ji}$.

We, then, find it computationally efficient to use the following commutation relations to recursively compute both the remaining $U(n)$ and the corresponding $U(2n)$ generator ME:

$$[E_{ij},E_{jl}]=E_{il}, \tag{56}$$

$$[E_{ij},E_{j\mu,l\mu}]=E_{i\mu,l\mu}, \tag{57}$$

with the latter relation being the special case of Equation 25.

The underlying algorithm has the following structure. The two outer loops go over the lower-triangular orbital indices row-by-row. In this way, commutation relations in Equations 56 and 57 allow for any non-elementary generator ME to be calculated from a ME one row above in the same column and an elementary generator ME in the same row. The first consecutive pair of the double-nested inner loops, for the given orbital indices, go over the global indices (in the order in which they have been calculated) of the ME and multiply together the pairs with identical "adjacent" GT basis vectors, that is, $\langle m|E_{i\mu,i-1\mu}|r\rangle\langle r|E_{i-1,j}|n\rangle$ and $\langle m|E_{i-1,j}|r\rangle\langle r|E_{i\mu,i-1\mu}|n\rangle$ in the case of the $U(2n)$ generators. The last double-nested inner loop goes over all the above-calculated parts of commutation relations and substract those corresponding to the same pair of GT basis vectors from each other according to Equations 56 and 57. Looping over the precomputed $E_{i,i-1}$ generator ME and using commutation relations allows one to avoid the level-by-level screening through the GT basis functions to estimate the nonzero elements. Although the presented algorithm contains the undesirable fourth-order nested loops, the two outer loops go over the number of orbitals constituting active space, which never grows too large and usually does not exceed a few tens for MCSCF calculations, so this does not make the overall code inefficient.

TABLE 1 Mulliken spin densities at the chromium and oxygen atoms of the Kremer's chromium dimer complex for the three different spin states, evaluated at the CASSCF theory level using spin-adapted GT configuration state functions

Atom	$S = 1$	$S = 2$	$S = 3$
$Cr_{1,2}$	0.986	1.972	2.958
$O_{1,2,3}$	0.007	0.014	0.021

Finally, the computed $U(2n)$ generator ME are passed to the subroutine that calculates spin density using Equation 5. We note that there is virtually no difference between calculating spin density from the $U(2n)$ generators following Equation 5 or directly from the adjoint tensor operator Δ using Equation 54 as $U(2n)$ are a simple function of Δ (Equation 34). Our choice was simply based on the fact that the subroutine evaluating spin density from the $U(2n)$ generator ME was already present in the code. We further note that the computational cost of calculating spin densities using the formalism by Gould et al. is equal to the cost of evaluating the one-particle generator matrix elements in terms of GT functions, that is, no additional costs are associated with the spin densities computation. Therefore, they can be easily evaluated with any active space tractable by the corresponding CI algorithm. We further note that one could as well apply the existing direct segment formulas for both the non-elementary $U(n)$ and $U(2n)$ operators. However, since one has only to loop over the precomputed nonzero generator matrix elements when using commutation relations, the additional computational costs are rather small and make very small difference overall.

As mentioned in introduction section, using the CSF as opposed to the SD basis is desirable to reduce large configuration spaces, restricting to a particular spin symmetry solution, which is especially useful when dealing with the manifold of high-spin states. We applied the implemented method to calculate spin densities for the $S = 1$, $S = 2$, and $S = 3$ states of the Kremer's tris-hydroxo bridged chromium dimer. Broken symmetry density functional theory (DFT) has been shown in Ref. [47] to give both the wrong spin ladder order and poorly reproduce the experimental zero field splitting values, while CASSCF yields both the correct order of states and coupled with the quasi-degenerate perturbation theory qualitatively reproduces the splitting values for all the spin states. DFT calculations have further failed to yield a symmetric spin density distribution.

We performed CASSCF calculations using SVP basis set and the same active spaces as in Ref. [47]: CAS(6,6) for $S = 1$ and CAS(6,10) for $S = 2$, and $S = 3$ (see the original paper for the active space composition). No effective core potential has been used for chromium atoms. We show the symmetric distribution of the spin density for the three spin states and its steady spread to the ligands from the chromium atoms with the growth of the spin quantum number in Figure 1. We further provide the symmetric Mulliken spin density values at the two chromium and three oxygen atoms in Table 1.

4 | DISCUSSION AND CONCLUSION

A few decades ago the UGA in quantum chemistry provided a unique instrument to perform large-scale CI electronic structure calculations in a basis of S^2 eigenfunctions. Somewhat later, a spin-dependent UGA based on the semi-simple Lie algebra has further pushed the limits of the field by allowing to compute spin-dependent properties such as spin density and make use of spin-dependent Hamiltonians. However, possibly due to its "heavy" formalism, there has been only one paper (based on the Shavitt's graphical aproach[48]), up to now, reporting a spin-dependent UGA implementation within a general electronic structure program.

In the current article, we report a new implementation of the (zero-order) spin-dependent UGA that allows the calculation of spin-dependent wavefunction properties for a spin-independent Hamiltonian. Specifically, we use it to calculate electronic spin density. In our implementation, we combine the Robb and Downward approach to calculate the $U(n)$ generator ME together with the Gould and Battle formalism to calculate the $U(2n)$ generator ME. An important feature of the Robb and Downward approach is that it utilizes Weyl tableaus, so that it can be used for arbitrarily restricted active spaces.[27]

Apart from presenting a practical implementation of the spin-dependent UGA, the second aim of this article is emphasize that the two different formalisms exist that lead to the same expression, namely Equation 54, giving the spin density as a function of contracted spin-independent one- and two-electron generators. In the works of Gould et al. this relation originates in the third-order polynomial identity (Equation 31) that the $U(n)$ generators satisfy and the properties of the $U(n)$ and $U(2)$ adjoint tensor operators, therefore, bearing a purely group theoretical nature. Remarkably, an equivalent expression in terms of one- and two-electron charge densities has been obtained (Equation 55) from a totally different formalism, namely from the studies of spin separation in the reduced density matrices by Whyman, Luzanov, and Mestechkin. We also acknowledge an elegant derivation of the same equation by Gidofalvi and Shepard using secondary quantization techniques.[45]

While these relationsips are interesting all, the more so being not intuitive. Moreover, they seem to have been forgotten in the general quantum chemistry community. However, as we have shown, there are important practical implications since they allow one to calculate spin density from a variational calculation involving a spin-free Hamiltonian.

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REFERENCES

[1] J. Paldus, *J. Chem. Phys.* **1974**, *61*, 5321.
[2] I. Shavitt, *Int. J. Quantum Chem.* **1977**, *11*, 131.
[3] I. Shavitt, *Chem. Phys. Lett.* **1979**, *63*, 421.
[4] I. Gelfand, M. Tsetlin, *Dokl. Akad. Nauk SSSR* **1950**, *71*, 825.
[5] I. Gelfand, M. Tsetlin, *Dokl. Akad. Nauk SSSR* **1950**, *71*, 1017.
[6] M. A. Robb, *Theor. Chem. Acc.* **2000**, *103*, 317.
[7] J. S. Battle, M. D. Gould, *Chem. Phys. Lett.* **1993**, *201*, 284.
[8] M. D. Gould, G. S. Chandler, *Int. J. Quantum Chem.* **1984**, *25*, 553.
[9] M. D. Gould, G. S. Chandler, *Int. J. Quantum Chem.* **1984**, *25*, 603.
[10] M. D. Gould, G. S. Chandler, *Int. J. Quantum Chem.* **1984**, *25*, 1089.
[11] M. D. Gould, G. S. Chandler, *Int. J. Quantum Chem.* **1984**, *26*, 441.
[12] M. D. Gould, G. S. Chandler, *Int. J. Quantum Chem.* **1985**, *27*, 787.
[13] M. D. Gould, J. Paldus, G. S. Chandler, *J. Chem. Phys.* **1990**, *93*, 4142.
[14] M. D. Gould, J. Paldus, *J. Chem. Phys.* **1990**, *92*, 7394.
[15] M. D. Gould, J. S. Battle, *J. Chem. Phys.* **1993**, *99*, 5961.
[16] R. D. Kent, M. Schlesinger, *Phys. Rev. A* **1990**, *42*, 1155.
[17] R. D. Kent, M. Schlesinger, I. Shavitt, *Int. J. Quantum Chem.* **1992**, *41*, 89.
[18] Z. Wen, Y. Wang, H. Lin, *Chem. Phys. Lett.* **1994**, *230*, 41.
[19] R. D. Kent, M. Schlesinger, *Phys. Rev. A* **1994**, *50*, 186.
[20] M. W. Lucht, M. D. Gould, *J. Chem. Phys.* **1995**, *103*, 5590.
[21] M. W. Lucht, *Phys. Rev. A* **1996**, *54*, 266.
[22] N. Flocke, M. Barysz, J. Karwowski, G. H. F. Diercksen, *Int. J. Quantum Chem.* **1997**, *61*, 1.
[23] T. L. C. Jansen, S. Rettrup, C. R. Sarma, J. G. Snijders, P. Palmieri, *Int. J. Quantum Chem.* **1999**, *73*, 23.
[24] X. Li, J. Paldus, *Theor. Chem. Acc.* **2014**, *133*, 1467.
[25] J. Paldus, M. D. Gould, *Theor. Chim. Acta* **1993**, *86*, 83.
[26] M. J. Downward, M. A. Robb, *Theor. Chim. Acta* **1977**, *46*, 129.
[27] D. Hegarty, M. A. Robb, *Mol. Phys.* **1979**, *38*, 1795.
[28] D. Datta, J. Gauss, *J. Chem. Phys.* **2015**, *143*, 011101.
[29] J. S. Battle, *Applications of the Unitary Group in Molecular Quantum Chemistry*, *Ph.D. Thesis*, University of Queensland, Brisbane, Queensland, Australia **1992**.
[30] A. V. Luzanov, *Theor. Exp. Chem.* **1985**, *21*, 329.
[31] T. Shiozaki, T. Yanai, *J. Chem. Theory Comput.* **2016**, *12*, 4347.
[32] G. E. Whyman, A. V. Luzanov, M. M. Mestechkin, *Theor. Math. Phys.* **1976**, *28*, 634.
[33] M. Moshinsky, *Group Theory and the Many-Body Problems*, Gordon and Breach, New York **1968**.
[34] G. E. Baird, L. C. Biedenharn, *J. Math. Phys.* **1963**, *4*, 1449.
[35] J. Paldus, in *Theoretical Chemistry: Advances and Perspectives*, Vol. *2* (Ed: H. D. Eyring), Academic, New York **1976**, pp. 131–290.
[36] M. A. Robb, U. Niazi, *Comput. Phys. Rep.* **1984**, *1*, 127.
[37] J. Paldus, in *Mathematical Frontiers in Computational Chemical Physics*, Vol. *15* (Ed: D. G. Truhlar), Springer-Verlag, New York **1988**, pp. 262–299.
[38] I. Shavitt, in *Mathematical Frontiers in Computational Chemical Physics*, Vol. *15* (Ed: D. G. Truhlar), Springer-Verlag, New York **1988**, pp. 300–349.
[39] H. S. Green, *J. Math. Phys.* **1971**, *12*, 2106.
[40] A. J. Bracken, H. Green, *J. Math. Phys.* **1971**, *12*, 2099.
[41] J. D. Louck, L. C. Biedenharn, *J. Math. Phys.* **1970**, *11*, 2368.

[42] J. E. Harriman, *Int. J. Quantum Chem.* **1979**, *15*, 611.

[43] A. V. Luzanov, G. E. Whyman, *Int. J. Quantum Chem.* **1981**, *20*, 1179.

[44] G. Klimko, A. Luzanov, *J. Struct. Chem.* **1988**, *28*, 633.

[45] G. Gidofalvi, R. Shepard, *Int. J. Quantum Chem.* **2009**, *109*, 3552.

[46] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, J. Bloino, B. G. Janesko, A. F. Izmaylov, A. Marenich, F. Lipparini, G. Zheng, J. L. Sonnenberg, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, P. V. Parandekar, N. J. Mayhall, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Development Version, Revision I.04+, Gaussian Inc., Wallingford, CT **2014**.

[47] S. J. Bennie, D. Collison, J. J. W. McDouall, *J. Chem. Theory Comput.* **2012**, *8*, 4915.

[48] S. Yabushita, Z. Zhang, R. M. Pitzer,*J. Phys. Chem. A* **1999**, *103*, 5791.

[49] M. Vacher, F. E. A. Albertani, A. J. Jenkins, I. Polyak, M. Bearpark, M. A. Robb, *Faraday Discuss.* **2016**, *194*, 95.

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